Organic Materials Chemistry

Date: 7 Mar 2013

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Integrity ★ Service ★ Excellence

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2013 AFOSR SPRING REVIEW

NAME: Charles Lee

BRIEF DESCRIPTION OF PORTFOLIO:

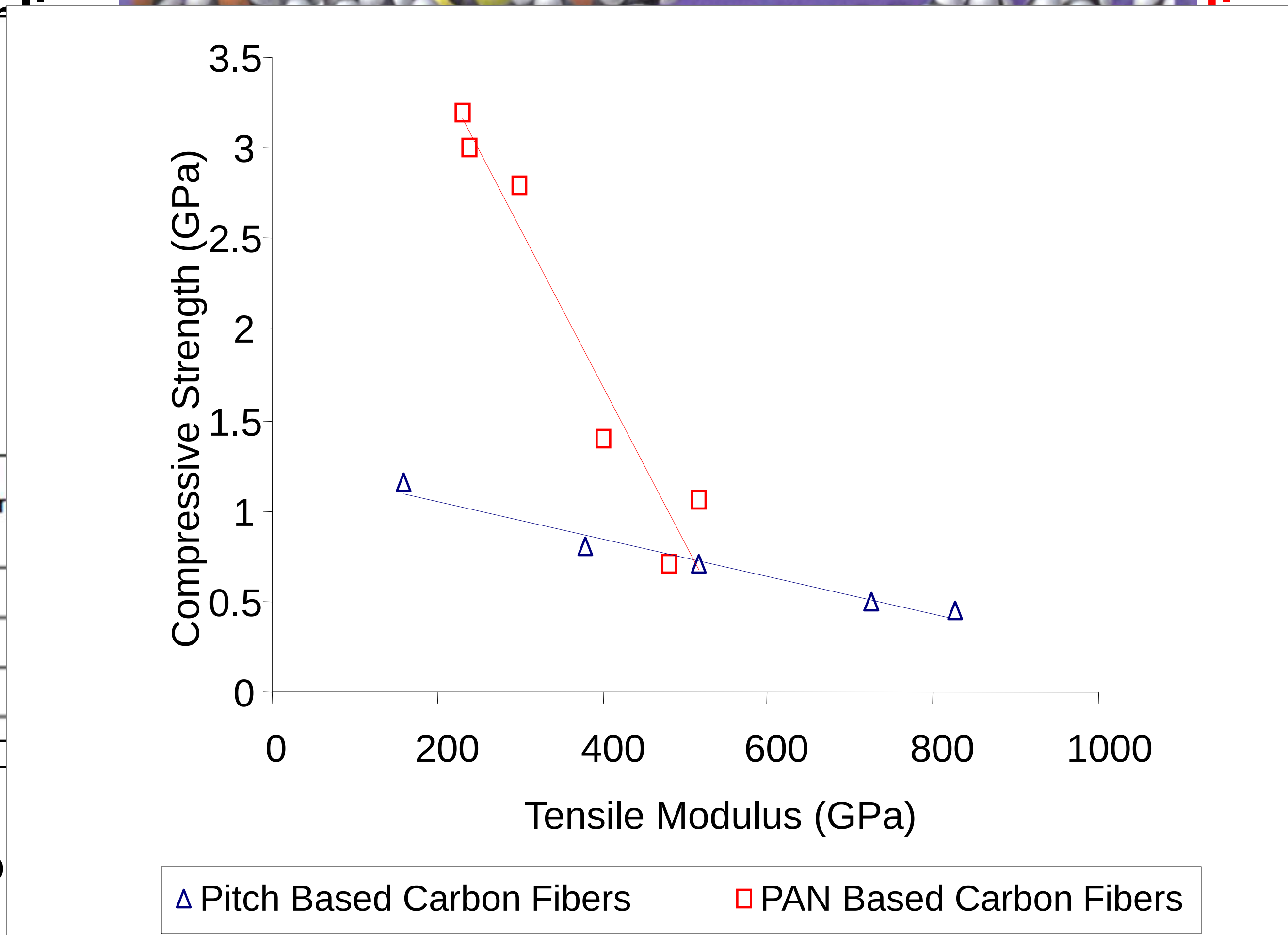
To exploit the uniqueness of organic/polymeric materials technologies for enabling future capabilities currently unavailable by discovering and improving their unique properties and processing characteristics

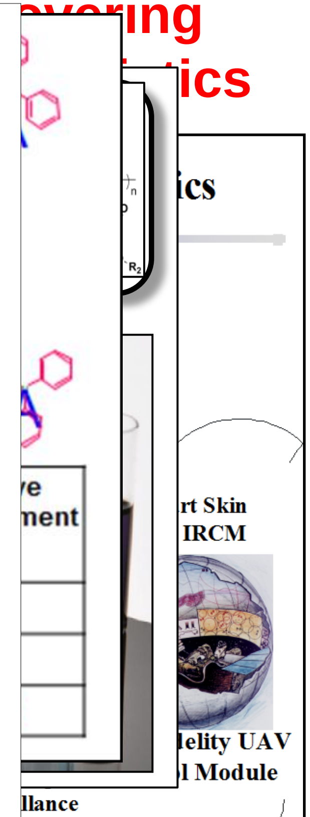
LIST SUB-AREAS IN PORTFOLIO:

Photonic Polymers/Organics
Electronic Polymers/Organics
Novel Properties Polymers/Organics
NanoTechnology

Organic Materials Chemistry Research Objective and Challenges

To exploit the u ... echnologies
for e ... ering
and ... ics





Challen
- Disc
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Approa
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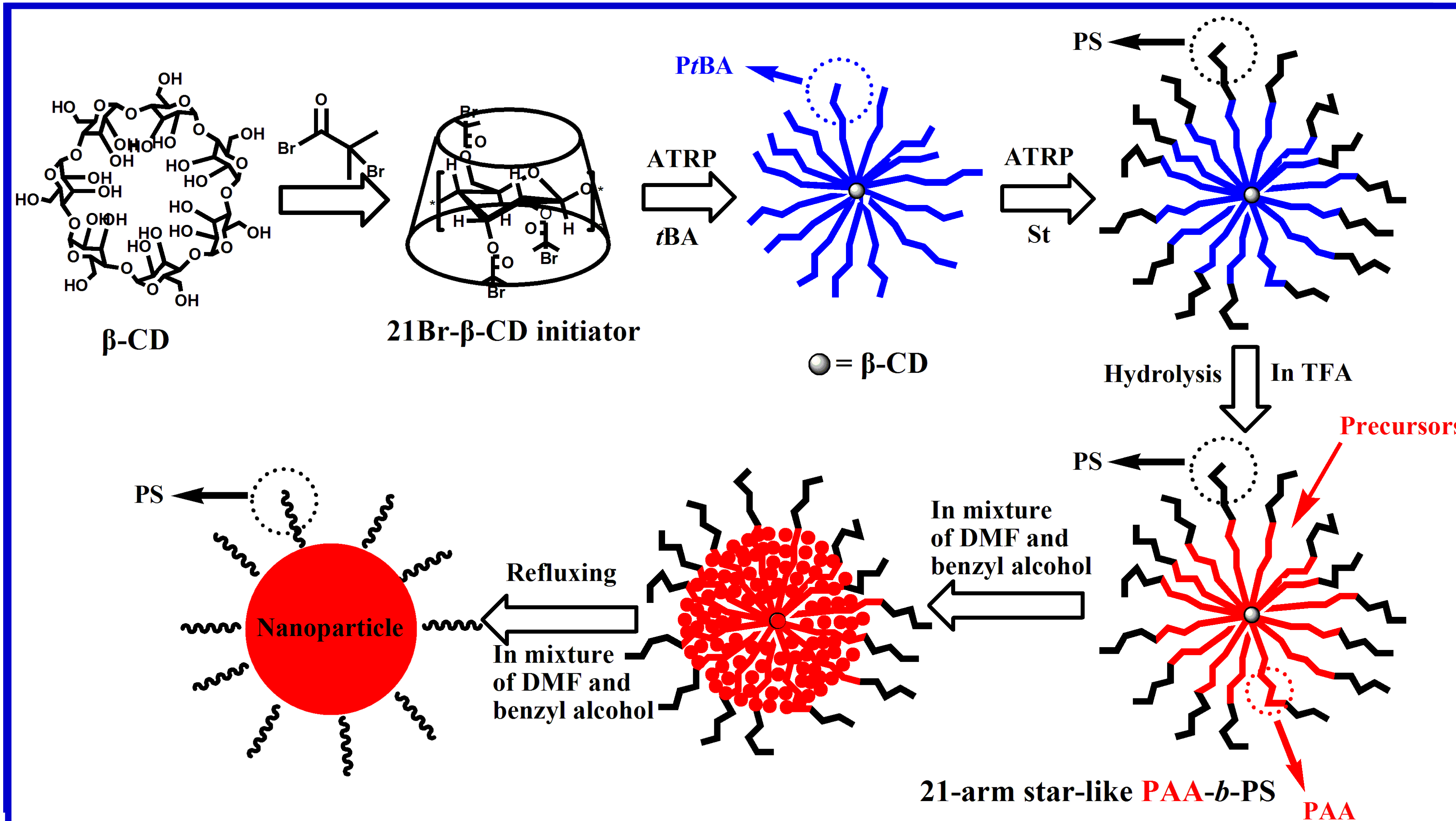
- Pro ... es
- Not applications specific, but often use applications to guide the properties focuses

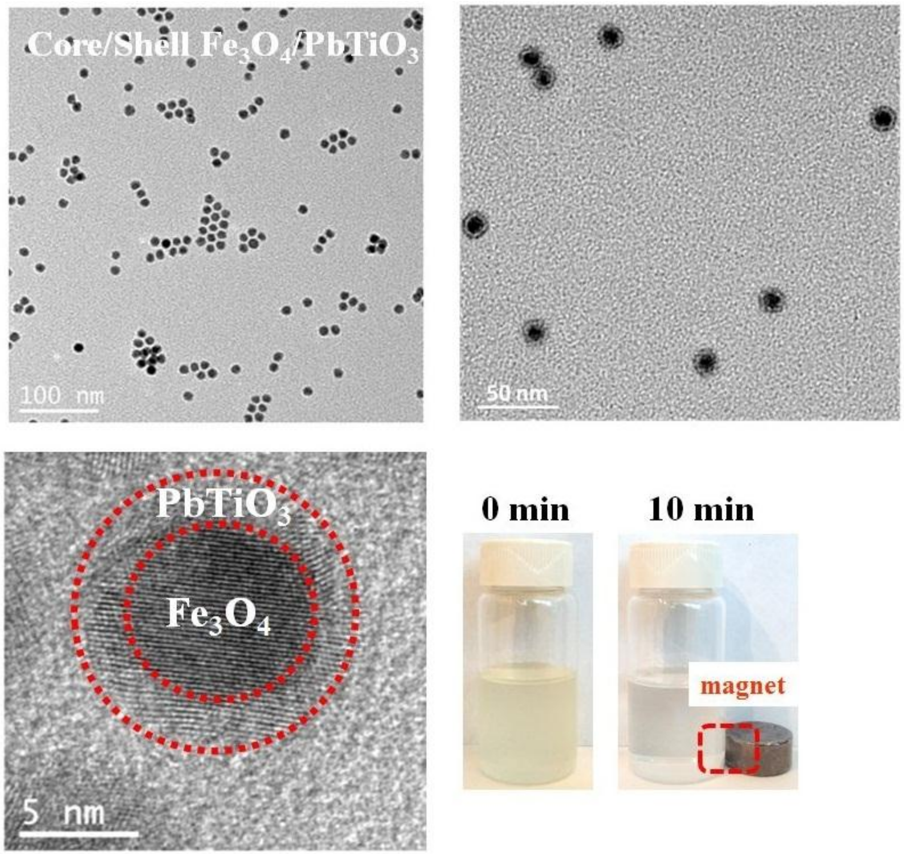
Self Assembled Micelle vs Covalently Bonded

	Small Molecule	Block CoPolymer	Star-Like Molecule
Au – Diameter (nm)	9±0.44	13±2	10.1±0.3
Grams/L	5.11	0.56	20.2
# Particles/L	6.9×10^{17}	2.5×10^{16}	2.0×10^{18}
Pt - Diameter (nm)	73±5.74	6.0±0.98	6.2±0.2
Grams/L	4.86	0.86	26.3
# Particles/L	1.1×10^{15}	3.6×10^{17}	1.1×10^{19}
Fe_2O_3–Diameter (nm)	16±1.49	10.8±2.98	10.1±0.5
Grams/L	2.94	1.81	36.2
# Particles/L	2.6×10^{17}	6.552×10^{17}	1.3×10^{19}
Cd-Se-Diameter (nm)	8.5±0.65	-----	9.9±0.3
Grams/L	0.98	-----	22.8
# Particles/L	5.2×10^{17}	-----	7.5×10^{18}
$PbTiO_3$-Diameter (nm)	-----	50±4.9	9.7±0.4
Grams/L	-----	2.12	31.2
# Particles/L	-----	4.1×10^{15}	7.5×10^{18}

NPs Synthesis by Novel Amphiphilic Star-Like Block Copolymers as Template



Core/Shell Nanoparticles – with Large Lattice Mismatch



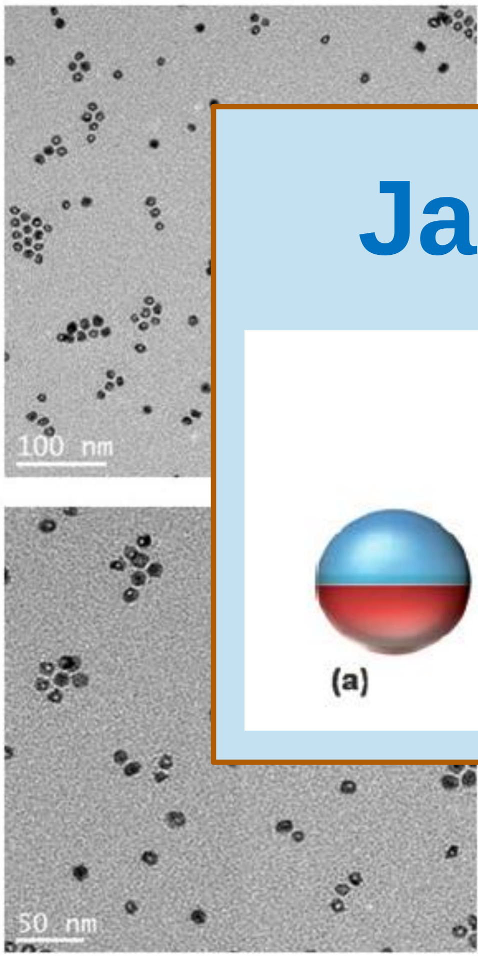
Core/shell nanostructures are *conventionally* obtained by dissimilar materials epitaxy, which requires moderate lattice mismatches (**<2%**) between the two different materials in order to obtain high-quality core/shell heterostructures, which would otherwise be difficult to obtain.

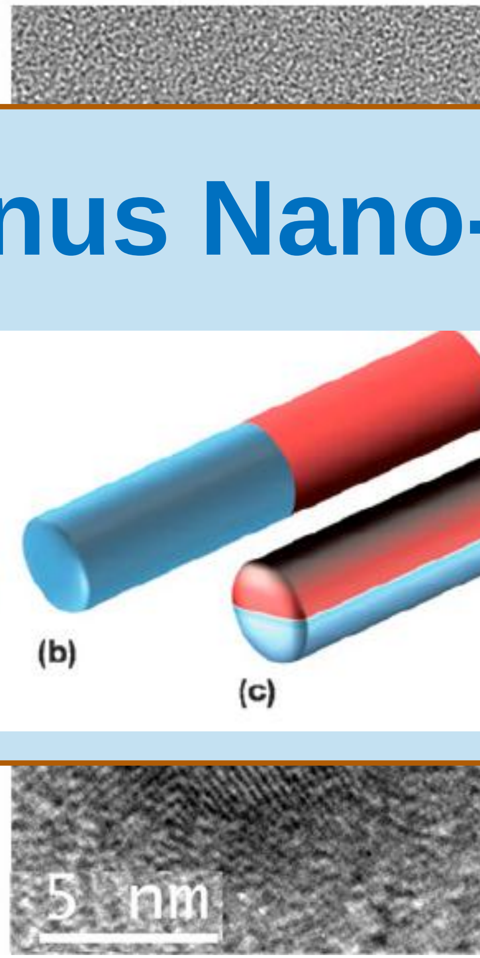
$Fe_3O_4/PbTiO_3$

D_{Fe3O4} = 6.1±0.3 nm (core)
D_{PbTiO3} = 3.1±0.3 nm (shell)

- **Despite more than 40% lattice mismatch between Fe_3O_4 and $PbTiO_3$, $Fe_3O_4/PbTiO_3$ core/shell nanoparticles can be readily crafted by this approach!!!**

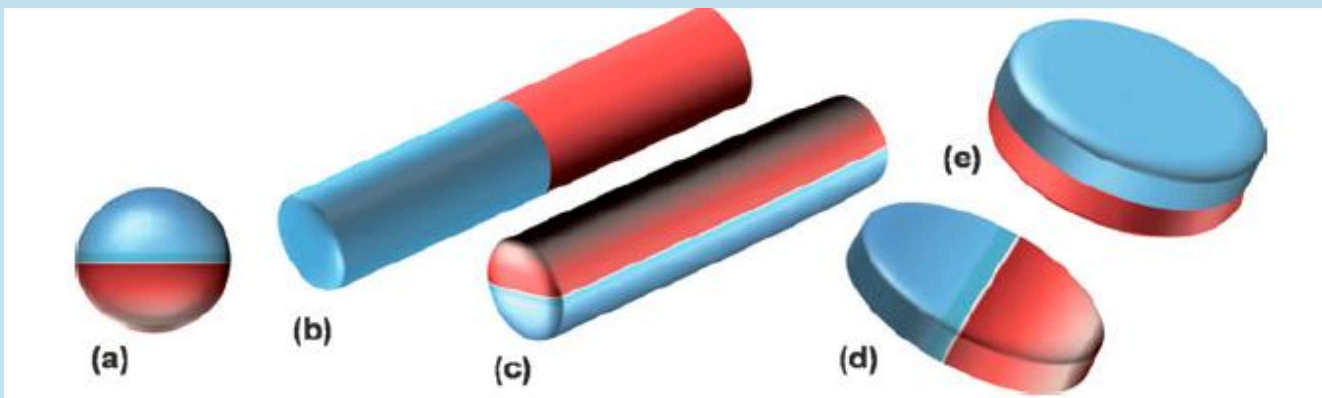
Hollow Nanoparticles – Au Nanoparticles





Hollow noble metal

Janus Nano-Particles



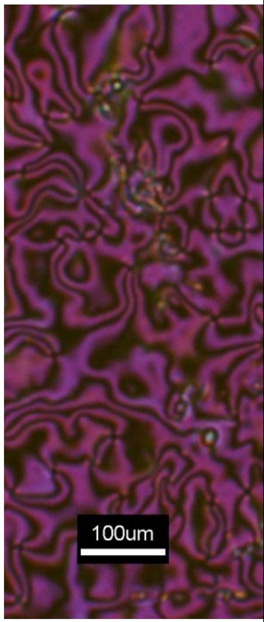
The diameter of hollow core = 5.6±0.4nm

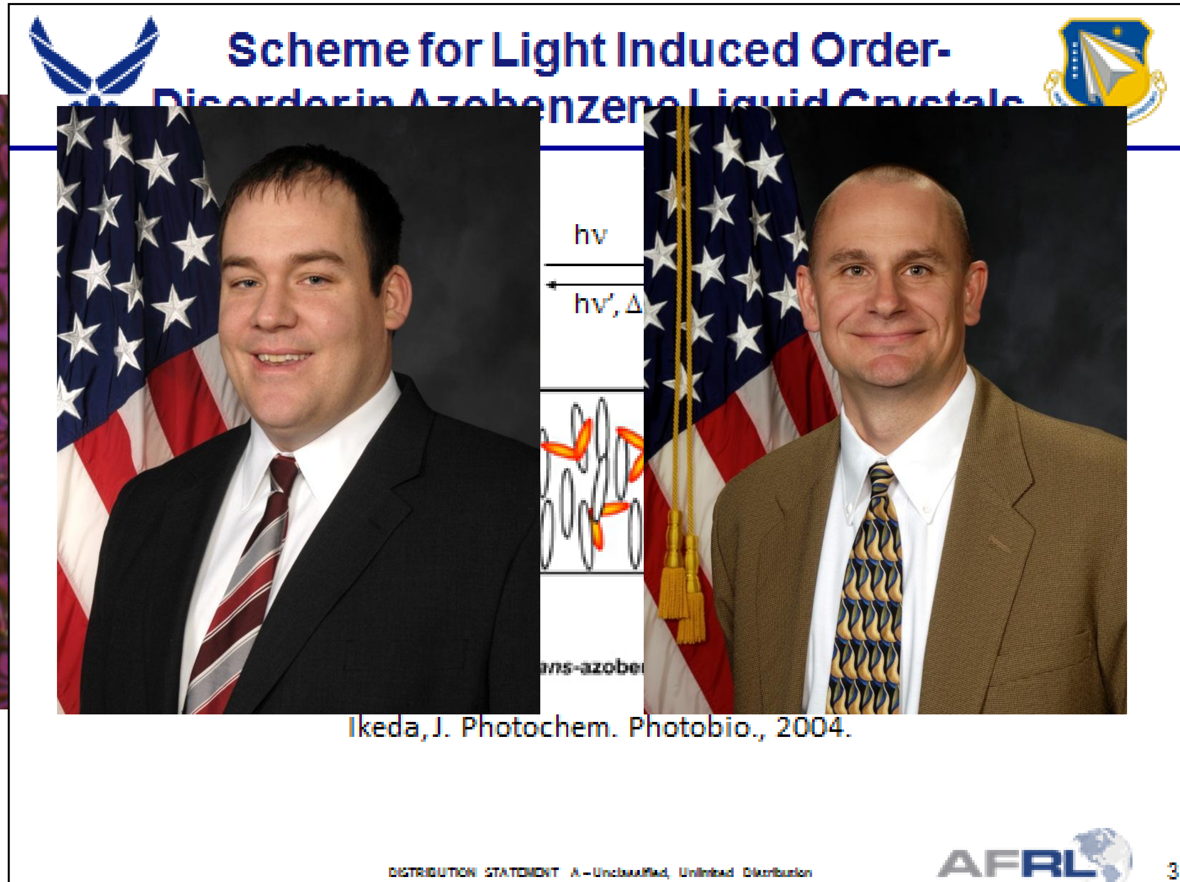
Phototropic liquid crystals

Tim White, Tim Bunning, AFRL/RX

"Phototropism": A term used to describe light induced phase changes in liquid crystals.

An example of

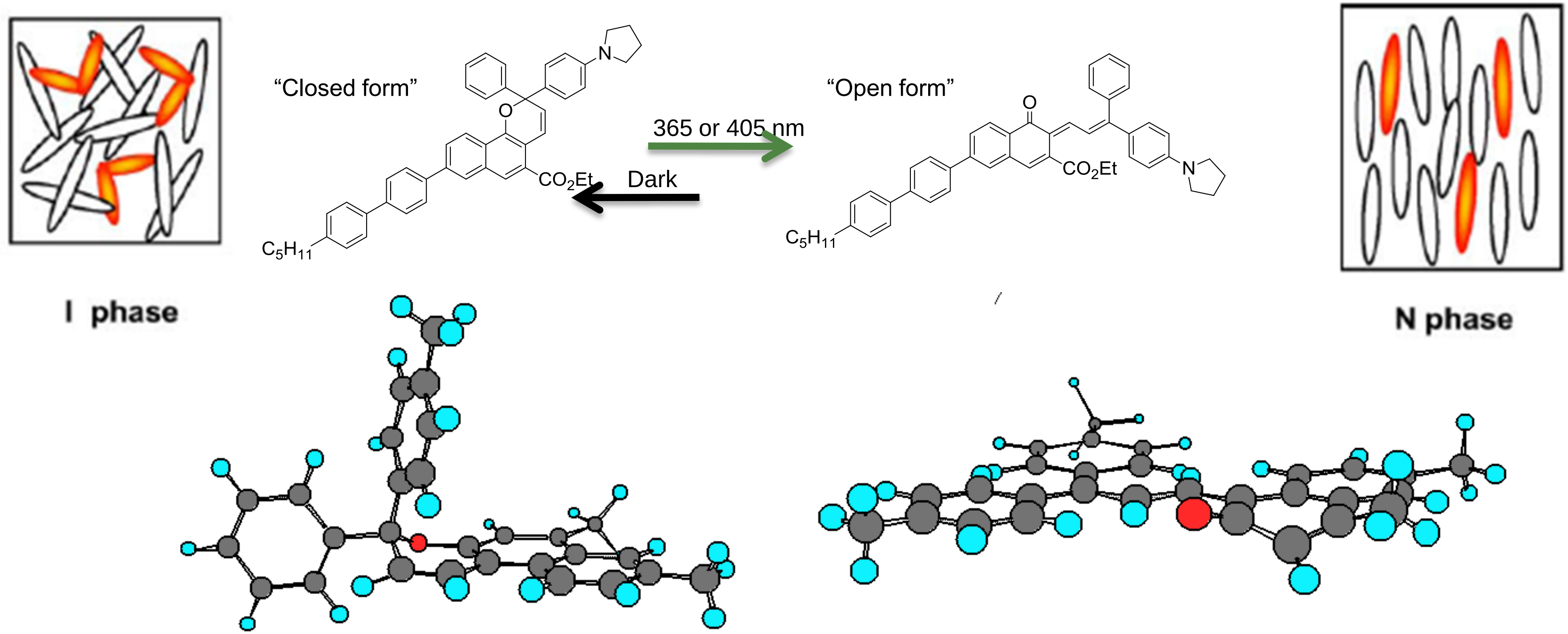




"Negative" phototropism – S (order parameter) decreases with light

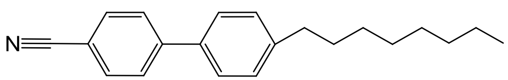
Light Induced Disorder-Order in Napthopyran (AMI15)/LC Mixtures

- New class of photochromic molecules that increase order upon light exposure employed for ***disorder-order transitions.***
- ***Demonstration of full gamut of Light Induced Phase Transitions***



In this case of “positive” phototropism, illumination increases the compatibility of the napthopyran as the molecular shape becomes planar and quasi-rod like aligning favorably with the liquid crystalline phases.

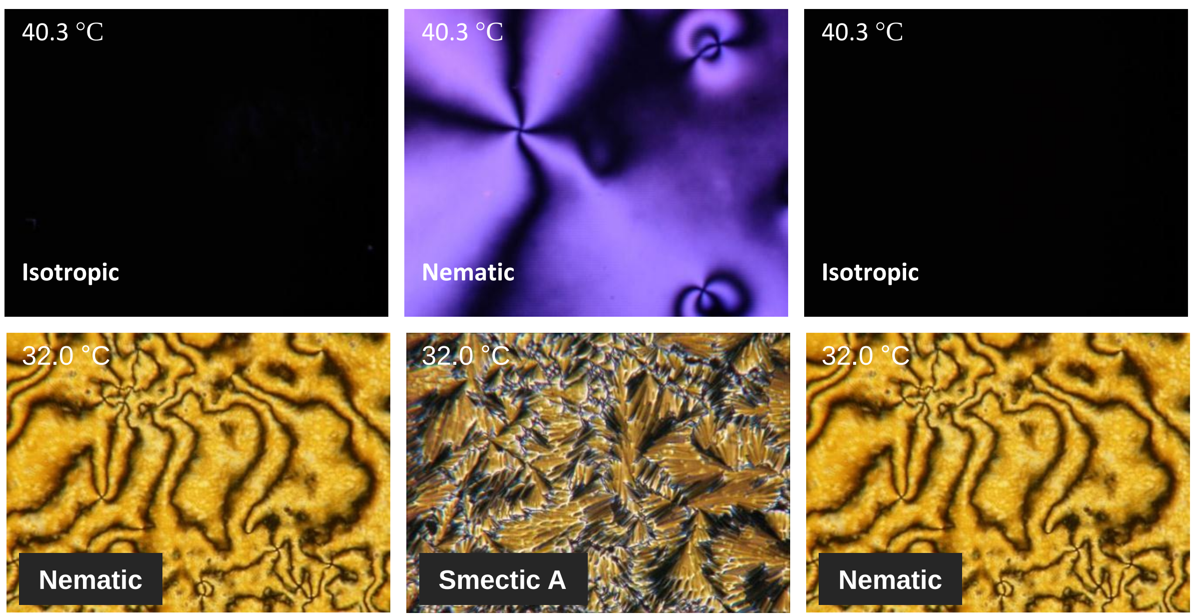
AMI15/8CB Mixture Shows Additional Transition



8CB

AMI15/8CB shows Photoinduced
- **Isotropic to Nematic Transition**
- **Nematic to Smectic A Transition**

Before light | **With light (365 nm)** | **After light**



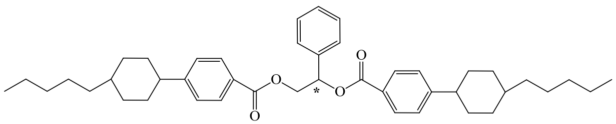
“Positive” phototropism – S (order parameter) increases with light

T. Kosa, L. Sukhomlinova, L. Su, B. Taheri, T.J. White, and T.J. Bunning,” Light Induced Liquid Crystallinity", Nature, 2012, 485, 347-349.

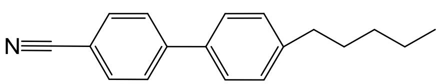
Different Phase Change with Chiral Dopant

AMI15/5CB/R1011 Mixture shows Photoinduced:

- **Isotropic to Cholesteric Phase Transition**

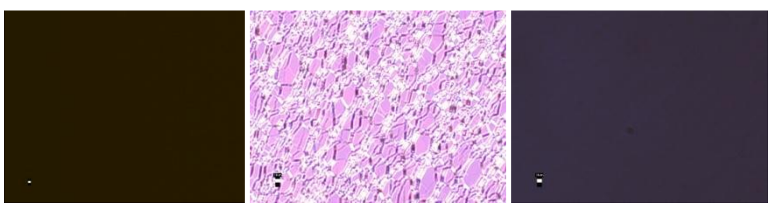


R1011 – a chiral dopant from Merck



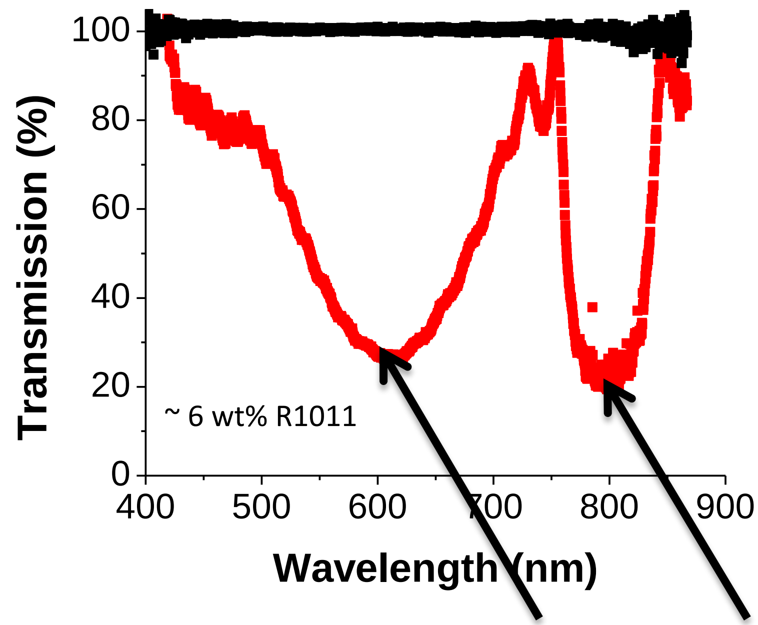
5CB

Before light | With light (365 nm) | After light



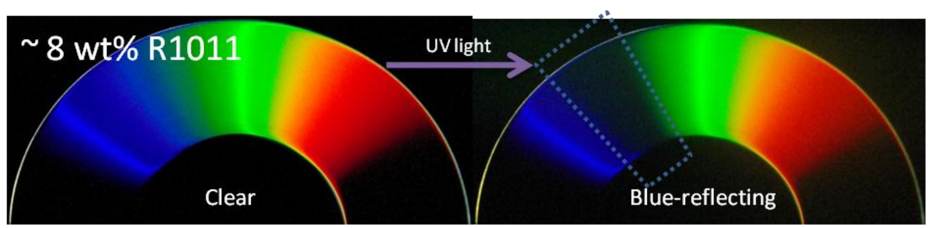
Data collected at AFRL/RX

Before irradiation – sample completely transmissive in VIS and NIR



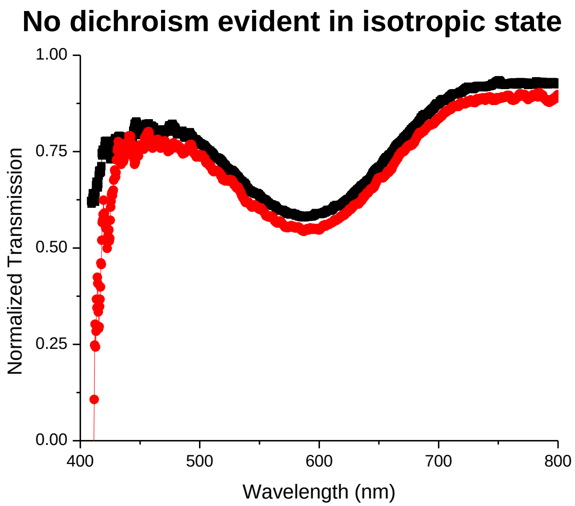
After irradiation – sample becomes both absorptive and reflective

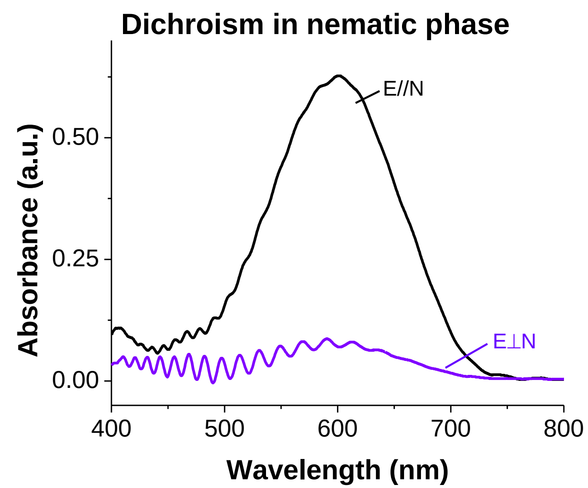
Data collected at AFRL/RX



Naphthopyran Phototropic Mixtures Unprecedented "Photo-dichroism"

For the Isotropic to Nematic Transition in AMI15/5CB Mixtures, Dramatic light induced changes in dichroic ratio from ~0 to 0.722



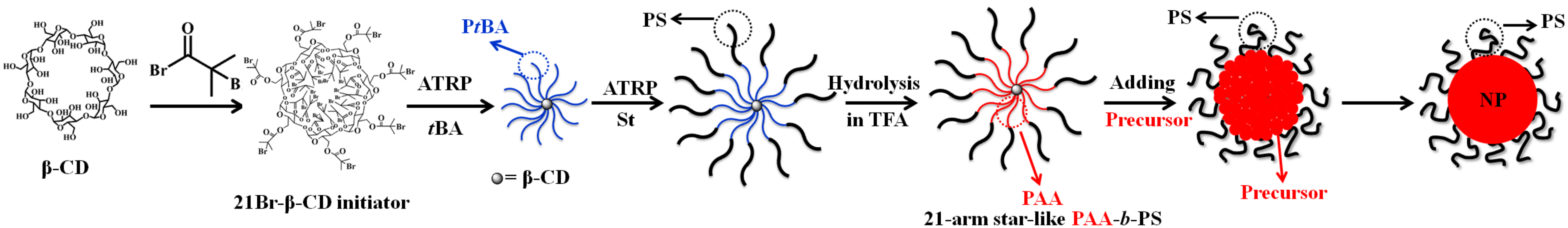


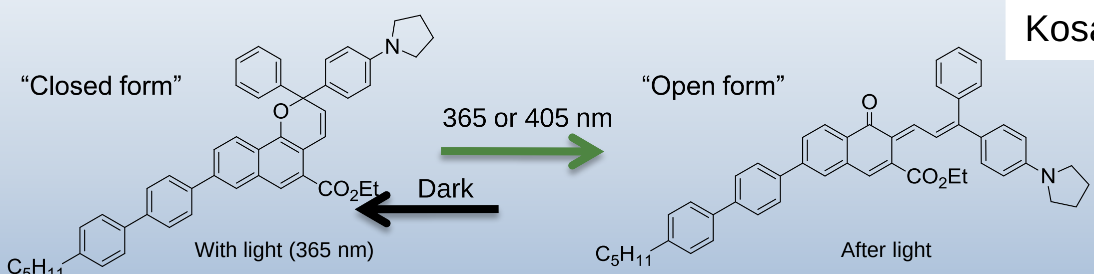
The mixture changes color and becomes polarized at the same time

(Plain Glasses become Polarized Sunglasses)

COE Georgia Tech/AFRL Joint Project

- **To craft novel *organic-inorganic nanocomposites* composed of Superparamagnetic Iron Oxide Nanoparticles (SPION) *intimately* and *permanently* connected with nematic liquid crystals (LCs) and chiral azo molecules with high helical twisting power (HTP) for many potential applications.**





Kosa and White et. al, Nature, 2012, (485), 347–349.

Light –induced liquid crystallinity

Color switching

potential for application in ***communication devices, molecular devices, light-controllable devices, optical display system, optical data recording, photo-optical triggers, polarizers, and reflectors, and electromagnetic sensors, etc.***

One-Dimensional Palladium Wires

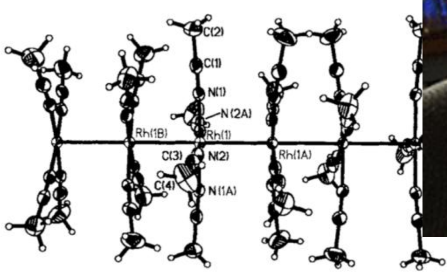
Tobias Ritter (YIP), Harvard U

Background on 1-D Metal Chains:

- Solid-state mixed-valence 1-D chains with Metal–Metal bonds
- Aqueous mi

-There are a few reports of infi
chains in the solid state with m
bonds.
-Not solution stable; Solid-stat

- **take several days or weeks**
- **low yield (usually 50% or less)**
- **small scale (< 100 mg)**

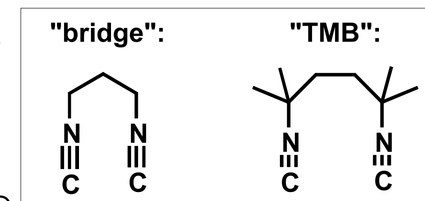


Angew. Chem. Int. Ed. **1969**, *8*, 35.
Angew. Chem. Int. Ed. **1996**, *35*, 2772.
J. Organomet. Chem. **2000**, *596*, 130.
Inorg. Chem. Commun. **2001**, *4*, 19.

$[Rh_2(TMB)_4]^{2\oplus}$

O_4
O

$h_2(bridge)_4]^{8\oplus}$



$h_2(bridge)_4]_2^{16\oplus}$

t 1-D metal chain
terized

nce (d^7-d^8) oligomers: Pt blues,
blues, Rh oligomers.

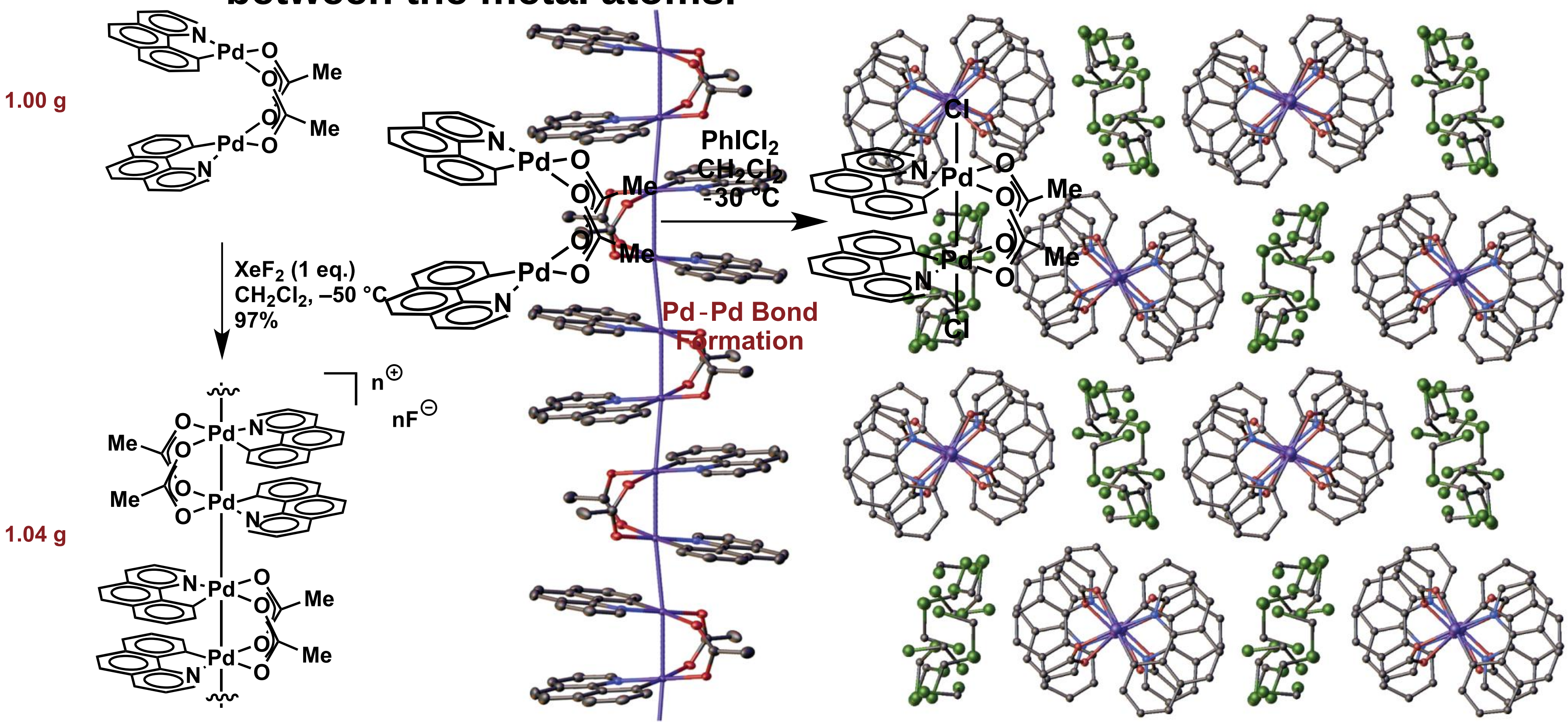
Chem. Ber. **1908**, *41*, 312.
Science **1982**, *218*, 1075.
Coord. Chem. Rev. **1999**, *182*, 263.
Angew. Chem. Int. Ed. **2001**, *40*, 4084.
J. Am. Chem. Soc. **1981**, *203*, 2220.

New Chemistry – Solution Processible Palladium Wires

From Dimers to Wires:

- Infinite Pd chains in solid state revealed by X-ray crystallography
- Rapid, High-Yielding, Gram-Scale, Solution Phase Synthesis

Oxidation of dipalladium(II) complexes with coordinating anions (Cl^-) leads to Pd dimers with covalent bond between the metal atoms.

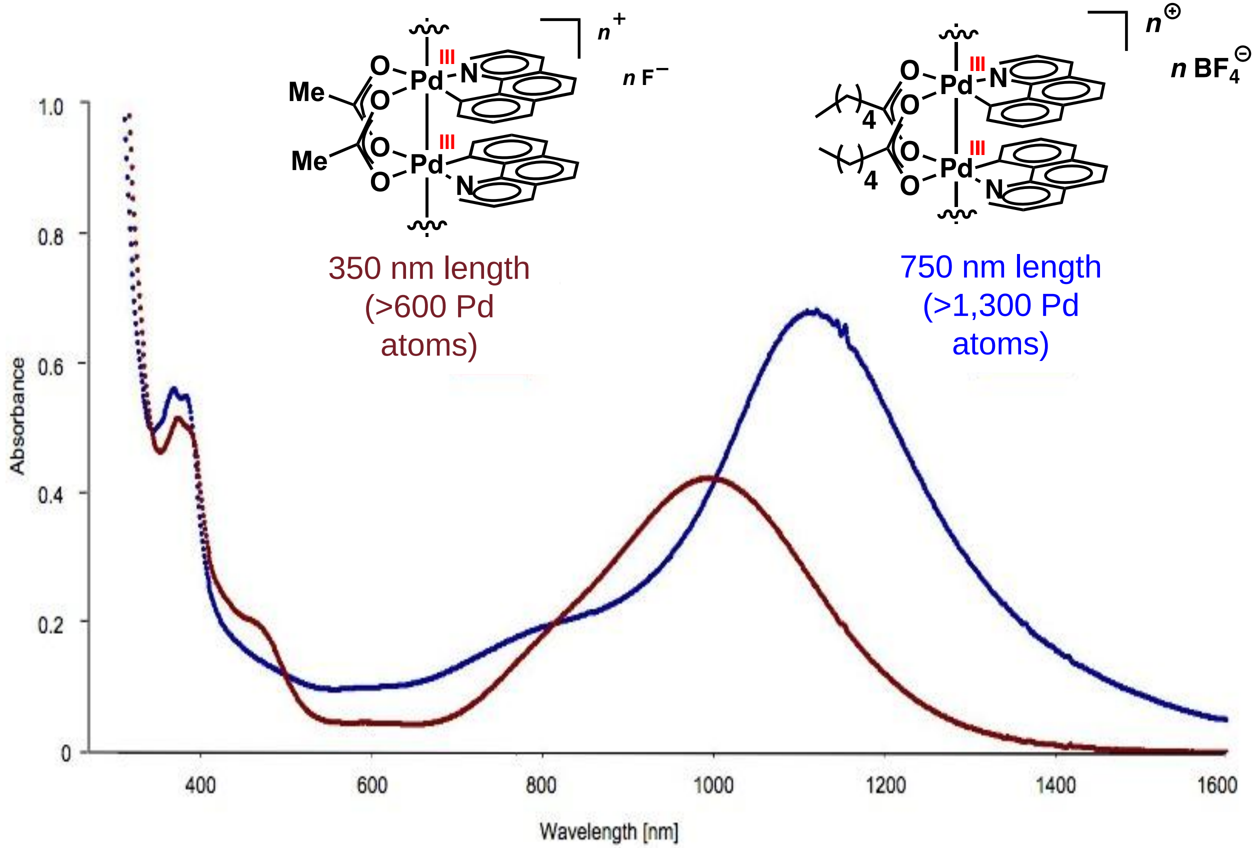


The polymerization occurs in solution in less than 5 minutes, giving pure material on large scale

Solution Stable 1-Dimensional Palladium Wire

1-D metal wires are predicted to display room temperature superconductivity

- Lengths up to 750 nm (>1,300 Pd atoms) observed in solution
- The longest solution-stable metal–metal bonded chain previously reported with assigned length contains 12 metal atoms‡.
- Choice of counter-Anion controls chain length
- Enabled efficient device fabrication, not possible with previous 1-D wires



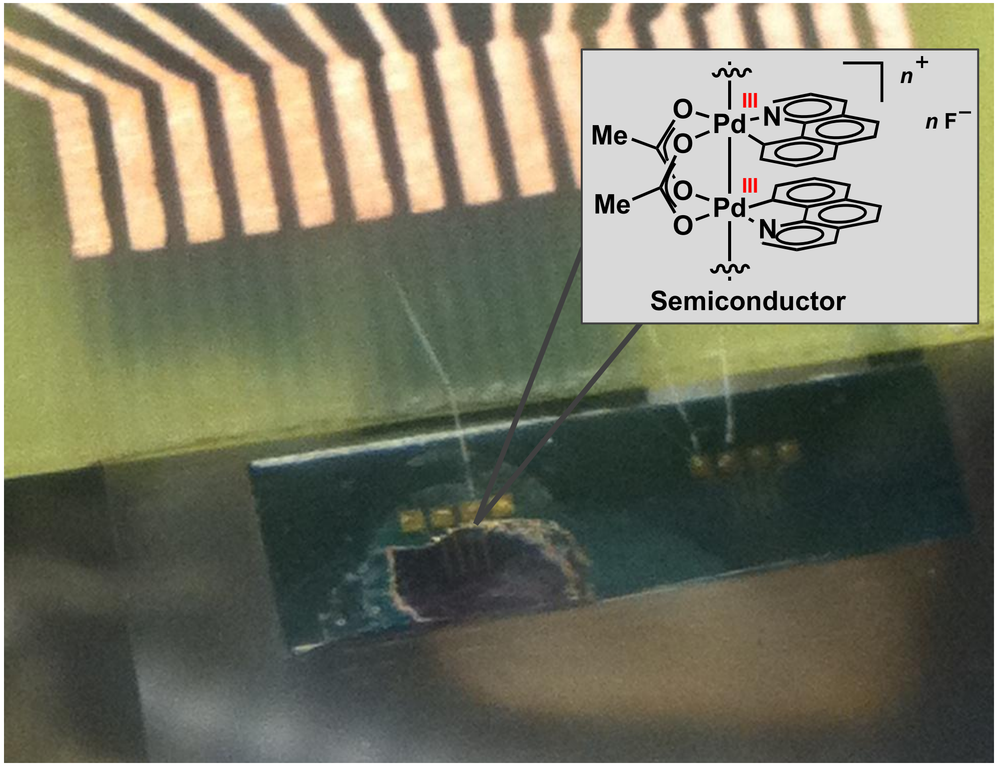
Nature Chem. **2011**, *3*, 949–953.
‡*J. Am. Chem. Soc.* **1981**, *203*, 2220–2225.

Four Point Probe Measurement

Thin-Film Conductivity:

- Solution processing capabilities allow for thin-film coating
- Four-point probe device used to measure conductivity of 1-D wire polymers film

Devices were fabricated using thin films of the 1-D wire polymers, which could be deposited from dichloromethane solutions either by drop casting or spin coating.

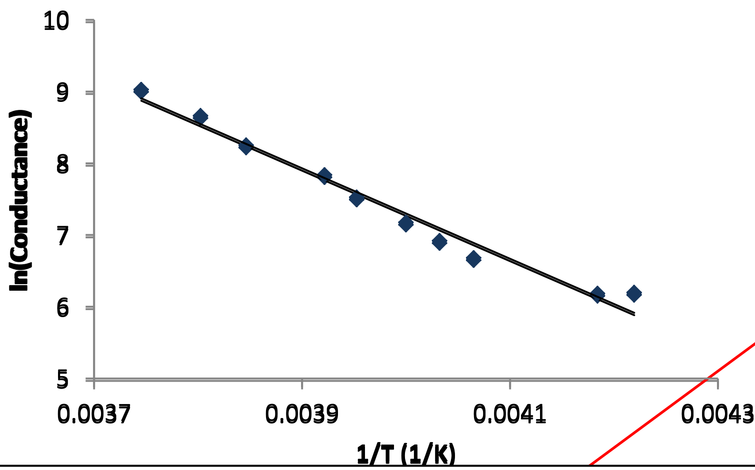


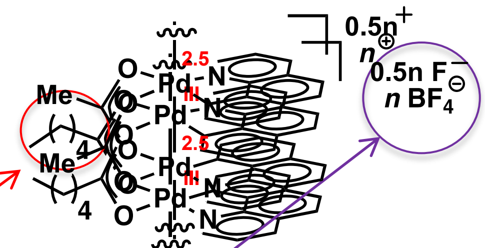
Nature Chem. **2011**, *3*, 949–953.

Tuning of Electronic Properties

Tuning Flexibility:

- **Side Group Solubility**
- **Counter Ion**
- **Pd Oxidation State**





Metallic Conductor Above 200 K

Semiconductor bandgap = 0.7 eV

Films based on Pd(2.5)display the first example of a transition to a metallic state observed at ambient pressure for a polymer based on 1-D metal wires.

Longer chains with less coordinating BF_4 anions display lower bandgap

Solution-stable 1-D metal wires with tunable conductive properties may have an impact on areas such as:

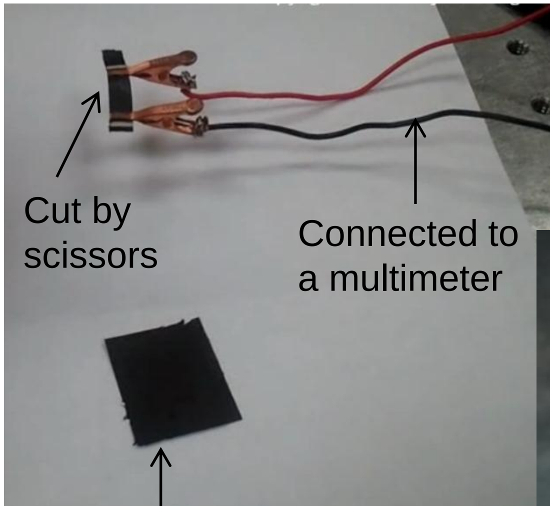
- **Next-Generation Solar Cells**
- **Molecular Sensors**
- **Molecular Wires for Nanoscale Circuits**

Nature Chem. **2011**, *3*, 949–953

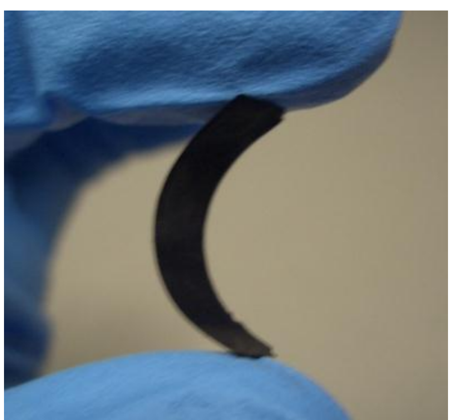
Power Generation with Body Heat

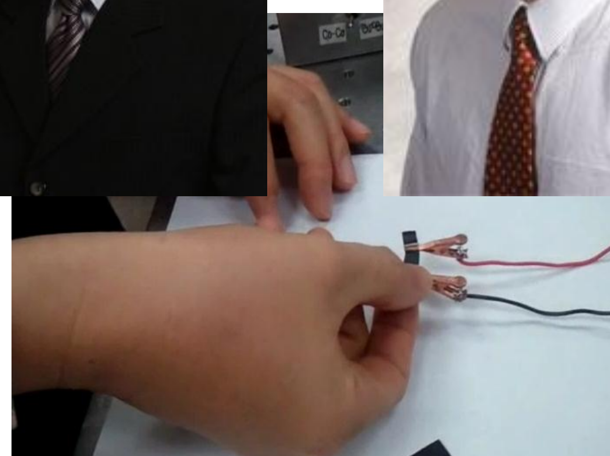
Choongho Yu & Jaime Grunlan, Texas A&M

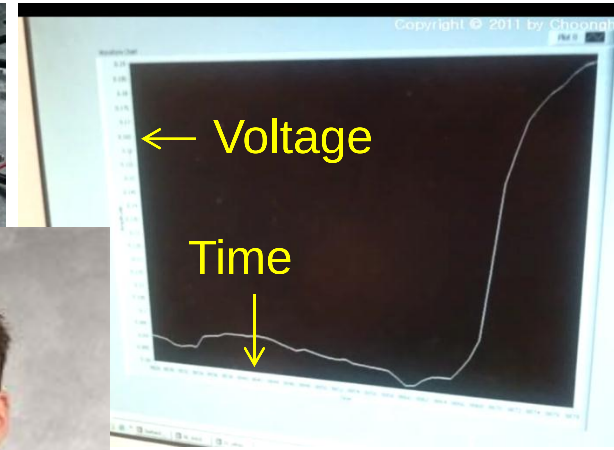
First demonstration of electricity generation from polymeric materials



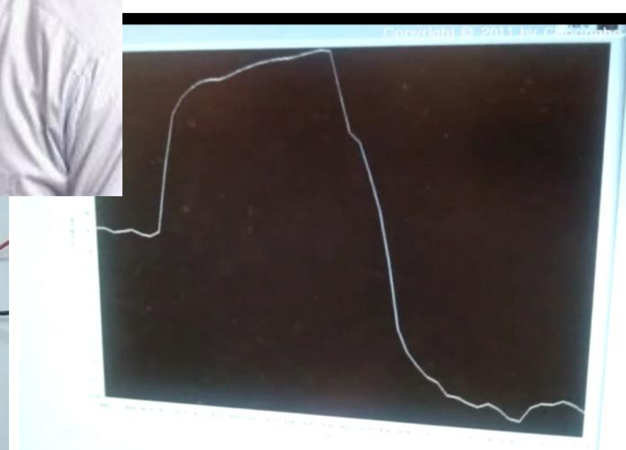
Flexible TE polymers







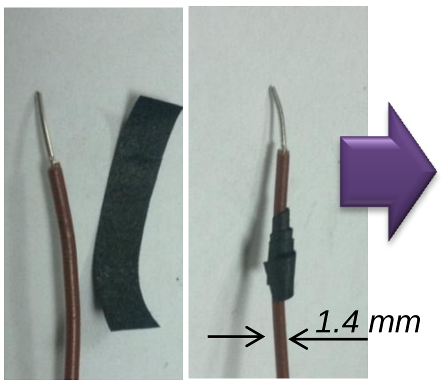
ltage –Time response



Air-stable fabric thermoelectric modules made of n & p-type composites

Objective: Demonstrate power generation & cooling with organic composites

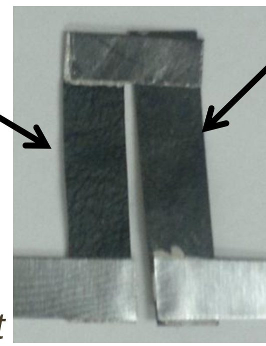
(1) Flexible composite



(2) Module fabrication

N-type

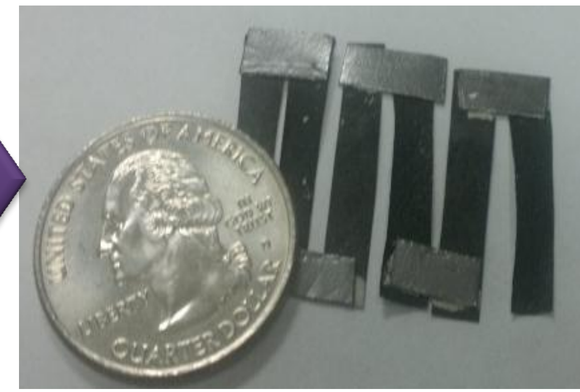
Carbon nanotubes + Poly-ethyleneimeine (PEI) + $NaBH_4$ treatment



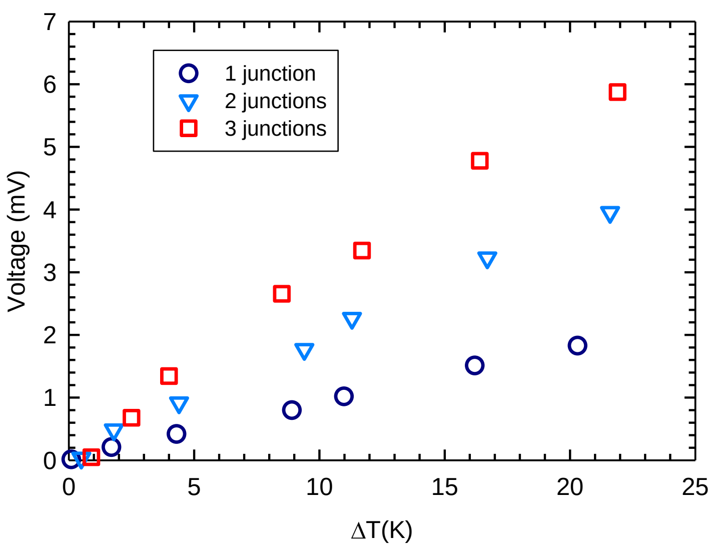
P-type

Carbon nanotubes + Paper (cellulose fibers)

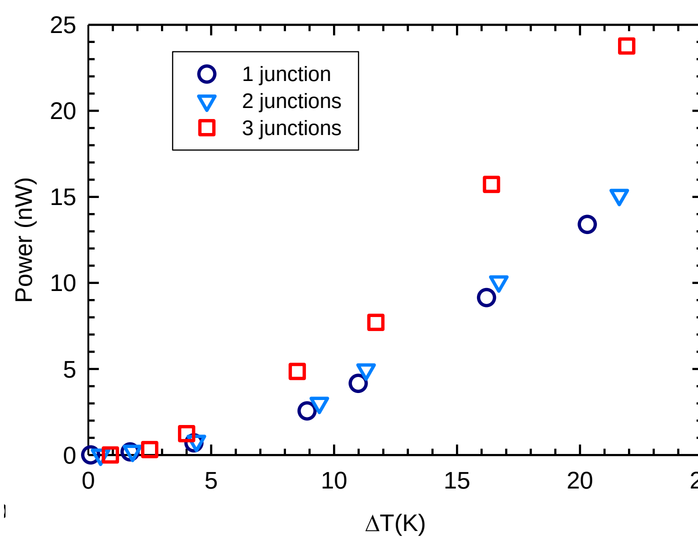
(3) Multiple junctions in series



Voltage output vs Temperature



Power output vs Temperature



Voltage and power are being increased by:

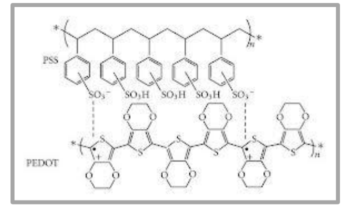
(a) stacking more layers;

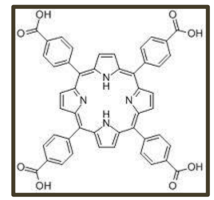
(b) connecting more modules

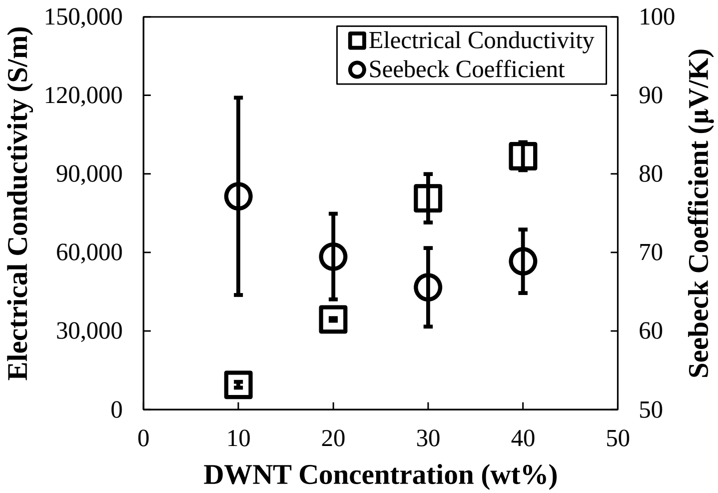
Improving Power Factor by Tuning P-type composites with multiple CNT stabilizers

Objective: Produce the highest possible power factor (PF) for fully organic, flexible composites

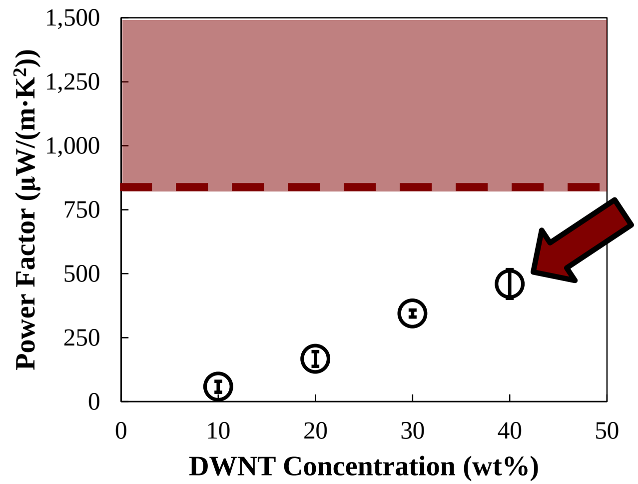
- Double-walled carbon nanotubes (DWNT) are stabilized with two different molecules in poly(vinyl acetate) latex:
  - **PEDOT:PSS (conductive)**
  - **TCPP (semi-conductive)**







Electrical conductivity increases with DWNT concentration; while the Seebeck coefficient remains relatively insensitive.



Highest PF ever reported for fully organic composite at ~500 μW(m·K²)!

The power factor ($S^2\sigma$) increases with DWNT concentration and is within an order of magnitude of traditional inorganics (maroon shaded region).

Different Module Design Concept

David Carroll, Wake Forest U.

Usin s and

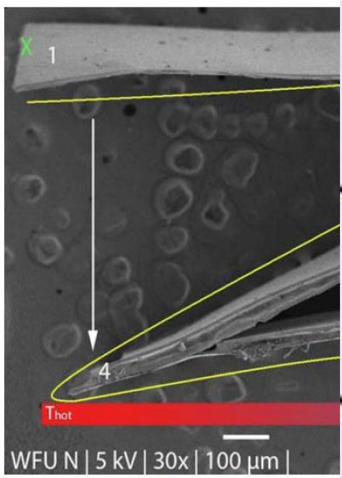
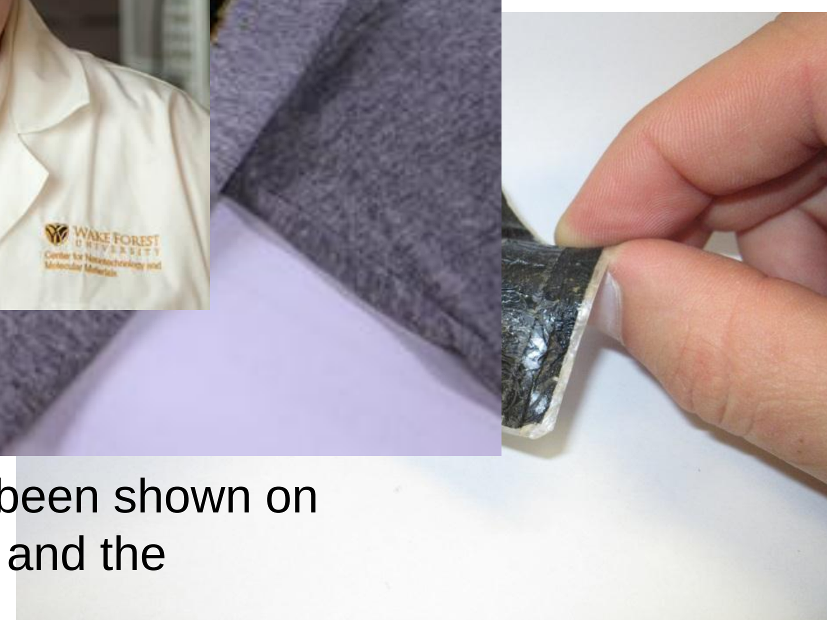


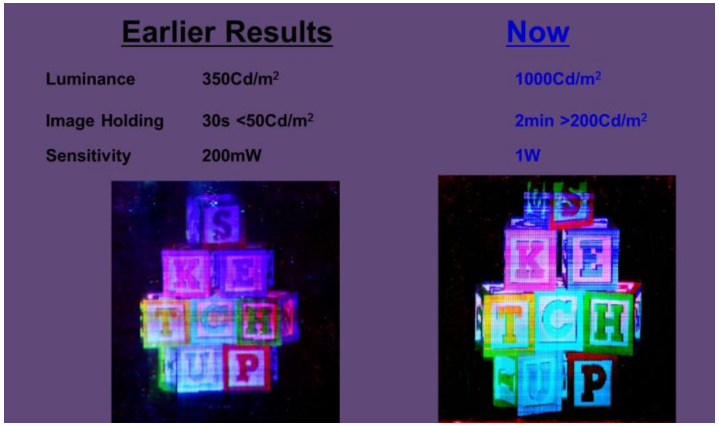
Figure 11: SEM image of multilayer C
in the p-type films (1), and –V in the n
films (4) adds the potentials in series. T



The garment has recently been shown on CNN International, CNBC, and the Discovery Channel.

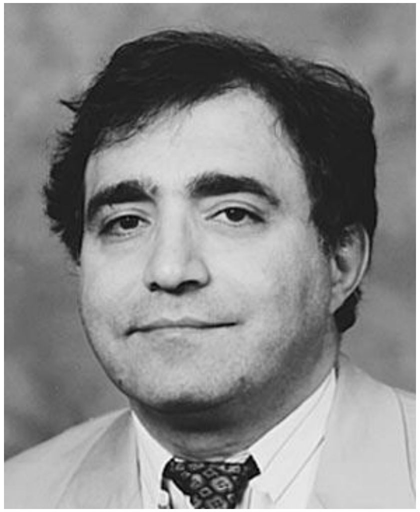
Photorefractive Polymers
Multi-TD's Interests

- **Laser Refraction**
- **Optical Signal Processing**
- **Wave Front Correction**
- **3D Holographic Display**
- **Image Correlation**

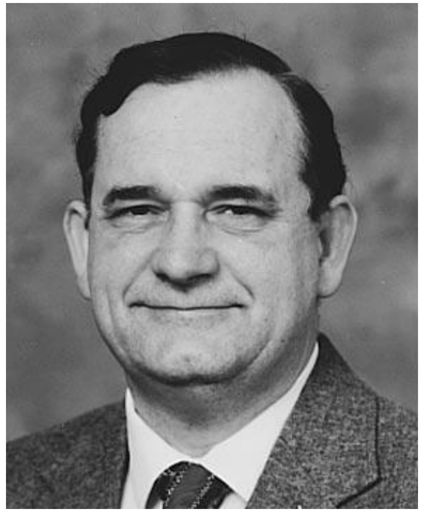


Two Beam Coupling Optical Correlation

Jed Khoury AFRL/RY (11RY01COR)

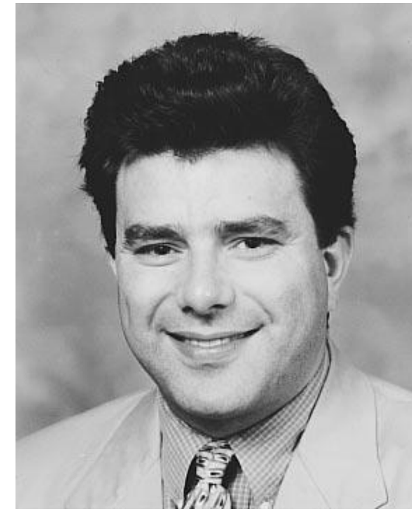


Jed Khoury

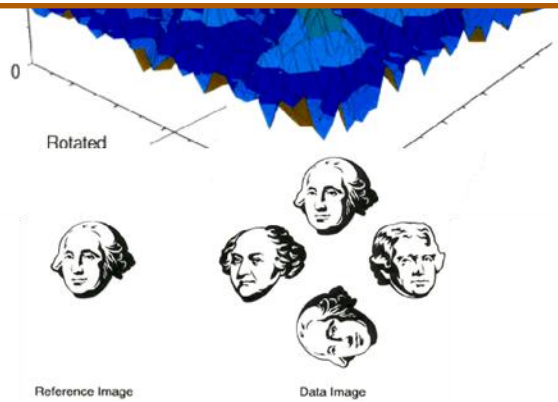


Charles Woods

Bahareh Haji-saeed



George Asimellis



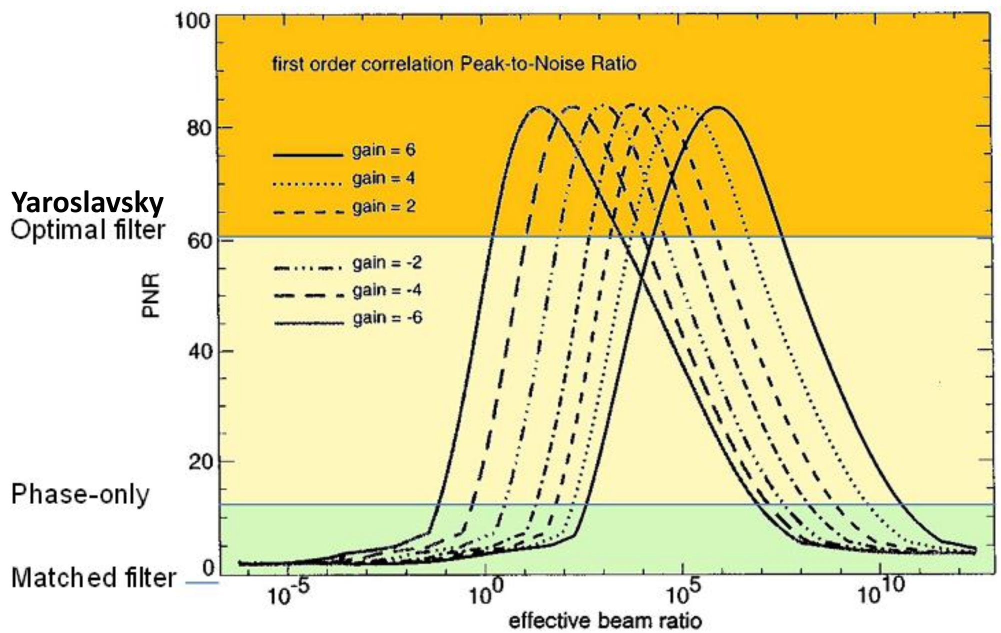
compression developed by AFRL/RY (Jed Khoury)

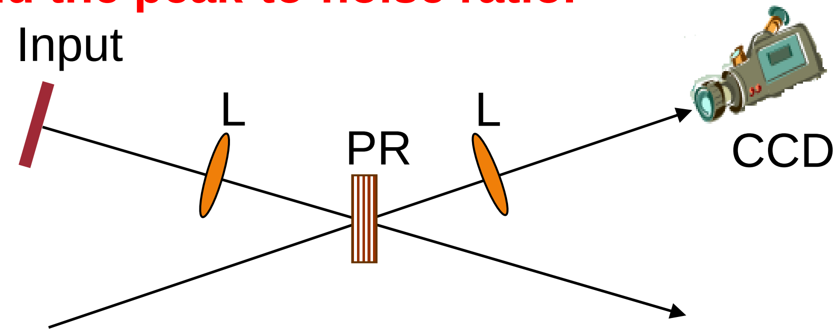
2. Organic photorefractive material that was developed by University of Arizona/Nitto Denko

Both efforts funded by AFOSR

Computer Simulation Comparing Two-Beam Coupling Correlation vs SOA Correlation Algorithms

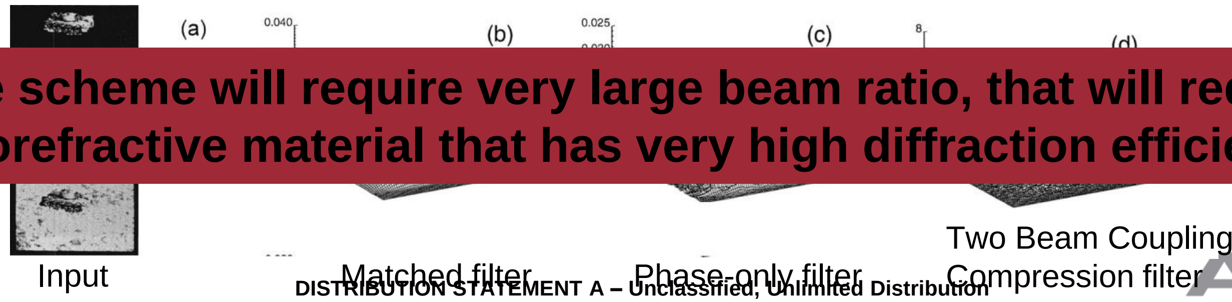
No correlation filter in the last 50 years, since the first correlation invented by Vander Lugt (1963), have been designed that can improve simultaneously the discrimination, the signal-to-noise ratio, and the peak-to-noise ratio.





Using input that has a lot of background noise, Two Beam Coupling Correlation is:

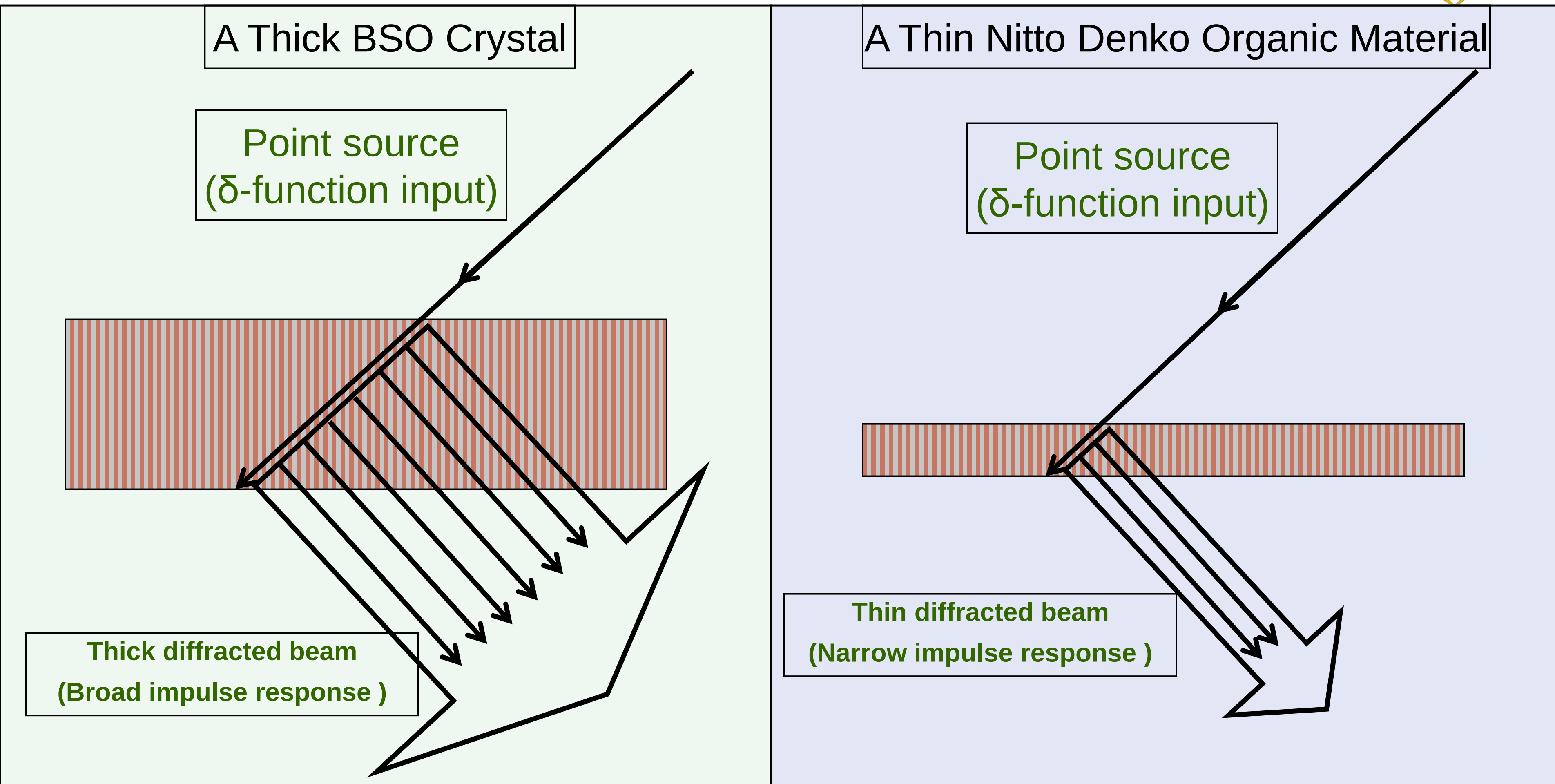
- **1.5X better than Yaroslavsky Optimal filter**
- **10X better than Phase-only filter**
- **superior to Matched filter (failed to recognize target)**



But the scheme will require very large beam ratio, that will require a photorefractive material that has very high diffraction efficiency.

BULK PHOTOREFRACTIVE CORRELATION VS THIN FILM PR POLYMER CORRELATION

Jed Khoury, AFRL/RY

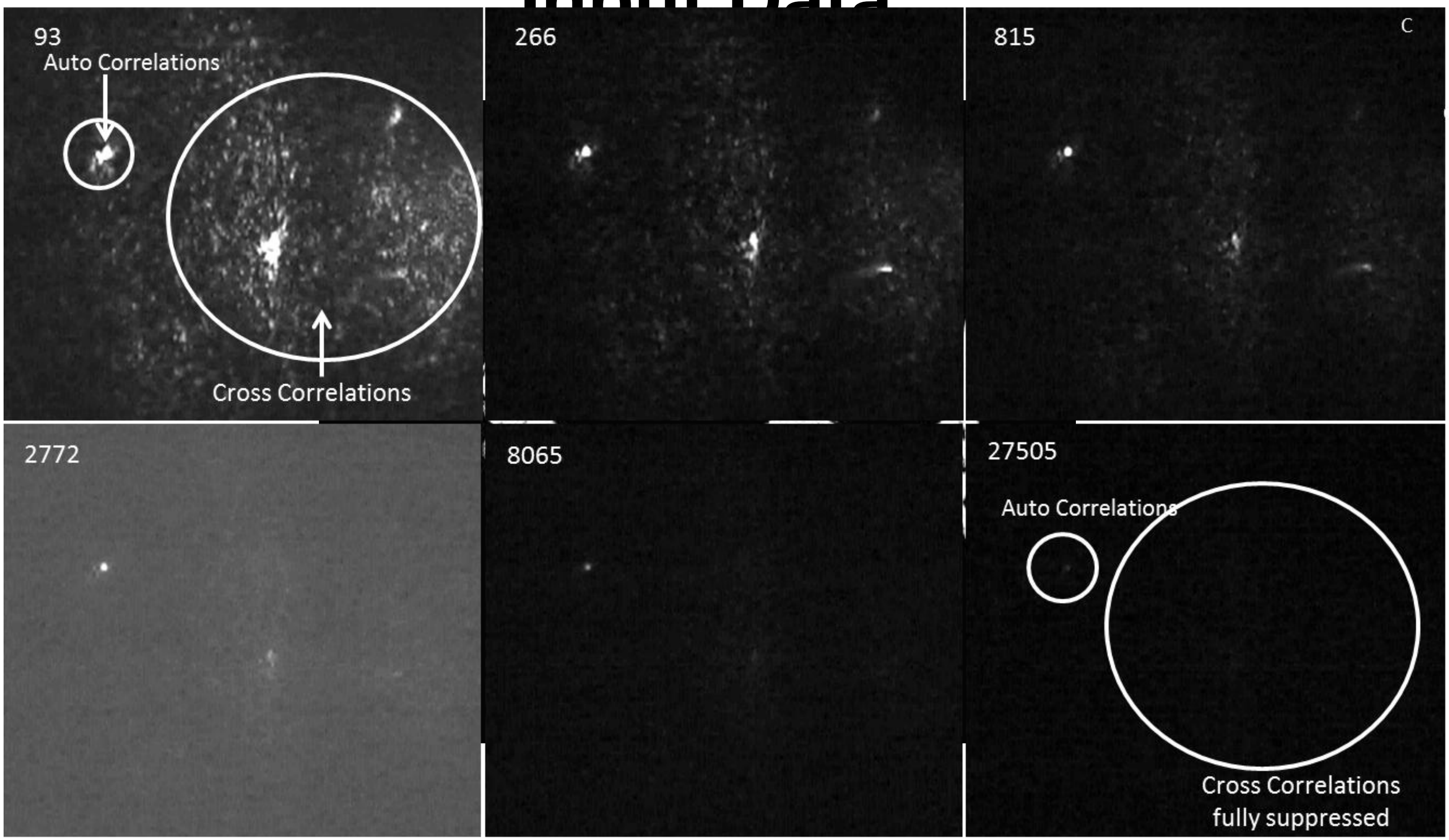


Dephasing Factor is small in thin film holographic materials.

Two Beam Coupling Experiment with PR Polymer Thin Film(1)

Dynamic range compression increases

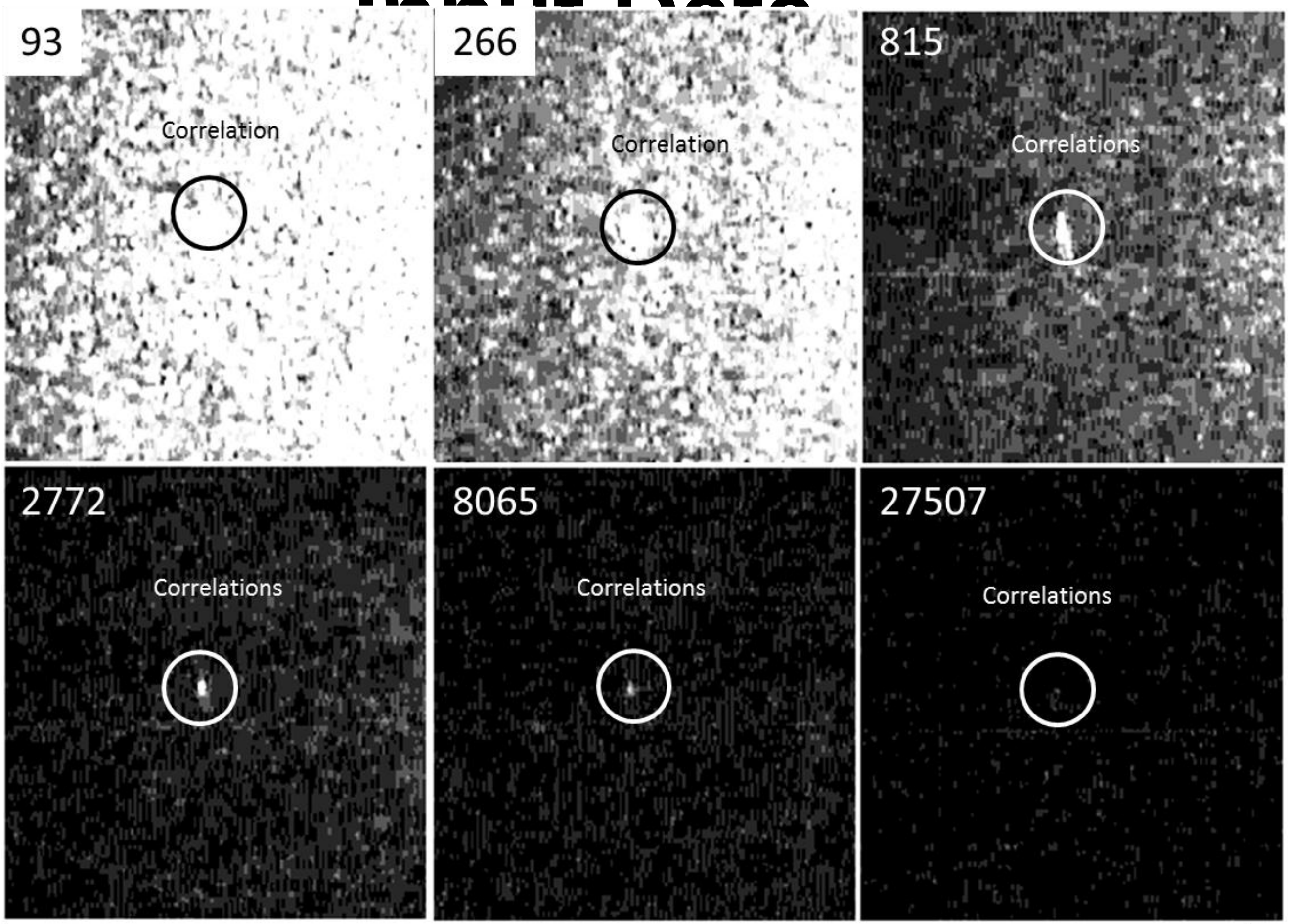
Input Data



Dynamic range compression increases

Two Beam Coupling Experiment with PR Polymer Thin Film (2)

Dynamic range compression increases

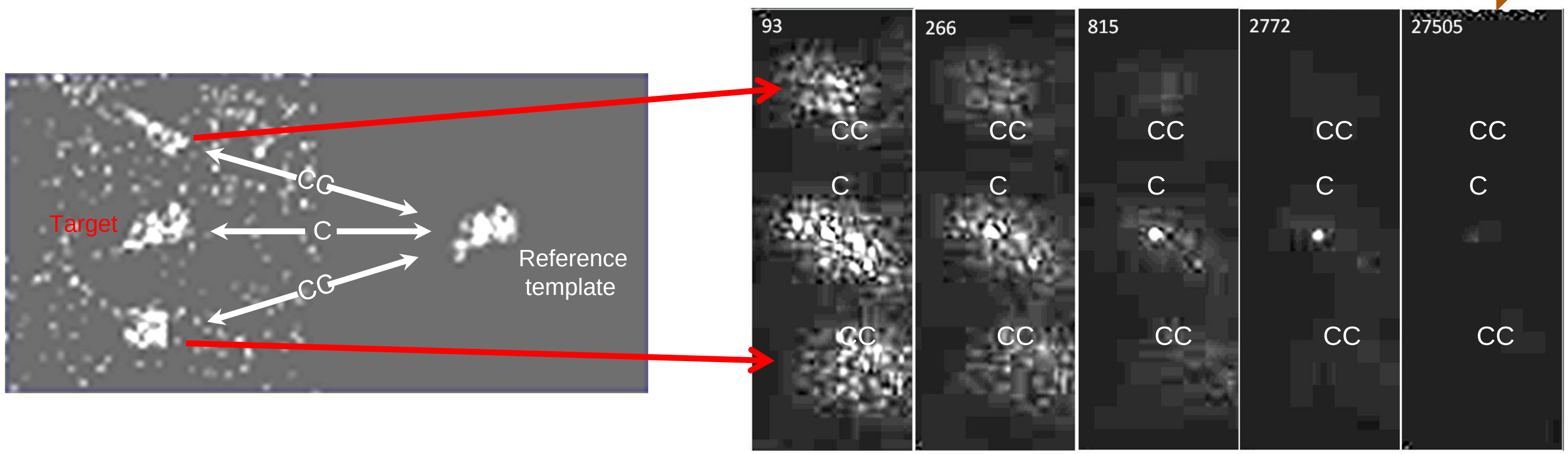


Dynamic range compression increases

Applied to Synthetic Aperture Radar Data

Low resolution images synthesized from the MSTAR data base

Dynamic range compression increases



The first correlation filter that can improve simultaneously the
- **SNR (100X)**
- **PNR,**
- **Discrimination (3 orders of Magnitude)**

Material Chemistry Makes It Possible!!!

Correlation filter that outperforms optimal digital correlation filters

Portfolio Trends

Decreasing Emphases:

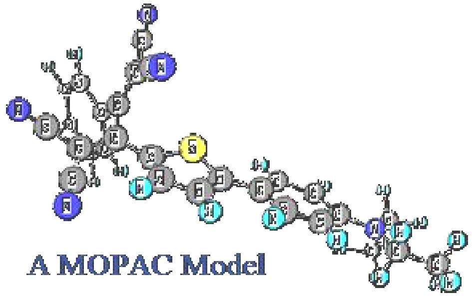
- -Organic Solar Cells
- -Organic Transistors

Increasing Emphases:

- -Self Assembly in Solid State
- -Radical, Spin and Excited State Controlled Properties

Summary

- **Program Focused on developing New and Controlled Properties**
- **Not applications specific, but often use applications to guide the properties focuses**
- **Scientific Challenges**
  - **- Discover New Properties**
  - **- Control Properties**
  - **- Balance Secondary Properties**
- **General Approaches**
  - **- Molecular Design**
  - **- Processing Control**
  - **- Establish Structure Properties Relationship**


A MOPAC Model